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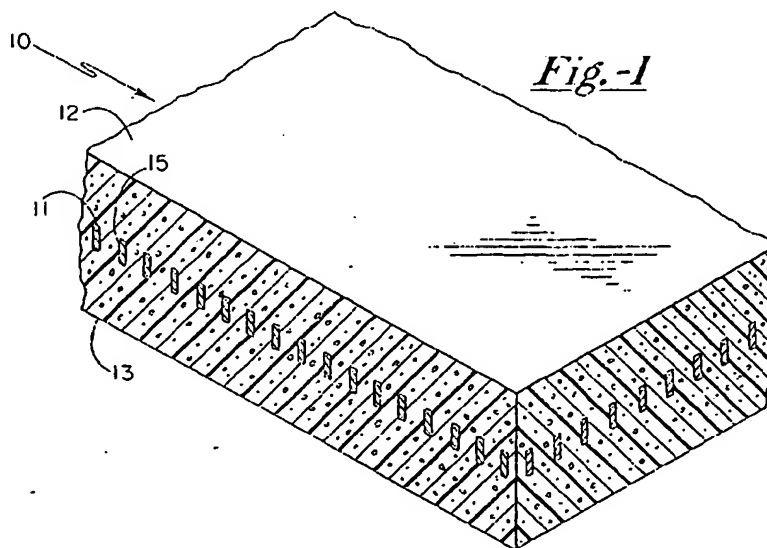
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(54) **Thermal interface pad utilizing low melting metal with retention matrix**

(57) A stabilized thermally conductive mechanical compliant laminate pad to be interposed between opposed surfaces of a generating semi-conductor device and a heat sink, with the laminate pad comprising upper and lower laminae on opposed surfaces of a central stabilizing apertured grid. The laminae are subjected to a compressive force at an elevated temperature until portions of the laminae extend through the apertures to

form a continuum. The laminae comprise a polymer matrix having a quantity of a low melting indium or gallium alloy and a thermally conductive particulate dispersed there through, with the polymer matrix being a hot wax or melt resin. With the upper and lower laminae positioned on opposed surfaces of a central stabilizing apertured grid a compressive load is applied to force portions of said laminae to pass through apertures in the mesh grid to form a continuum.

*Fig. -1***EP 1 414 063 A2****BEST AVAILABLE COPY**

Description

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application is a continuation-in-part of our co-pending application Serial No. 09/946,879, filed September 5, 2001, entitled "MORPHING FILLERS AND THERMAL INTERFACE MATERIALS"; which application Serial No. 09/946,879 was a continuation-in-part of our prior co-pending application Serial No. 09/690,994, filed October 17, 2000, entitled "METHOD OF PREPARING THERMALLY CONDUCTIVE COMPOUNDS BY LIQUID METAL BRIDGED PARTICLE CLUSTERS", which application Serial No. 09/690,994 is a continuation-in-part application of our parent application Serial No. 09/543,661, filed April 5, 2000, entitled "METHOD OF PREPARING THERMALLY CONDUCTIVE COMPOUNDS BY LIQUID METAL BRIDGED PARTICLE CLUSTERS", now U.S. Patent No. 6,339,120, all of which are assigned to the same assignee as the present application.

BACKGROUND OF THE INVENTION

15 [0002] The present invention relates generally to an improved mechanically stabilized thermally conductive interface pad for transferring thermal energy from a heat generating semiconductor device to a heat dissipator such as a heat sink or heat spreader. More specifically, the present invention relates to such an interface which comprises a laminate pad with upper and lower thermally conductive laminae positioned upon and extending through apertures from opposed surfaces of an open mesh grid. In other words, portions of each of the opposed laminae extend through apertures in the stabilizing mesh grid to form a continuum, thus enhancing both mechanical stability and heat transfer efficiency without the creation of additional thermal interfaces.

20 [0003] The upper and lower laminae preferably comprise formulations of highly thermally conductive polymer compounds such as a polymeric matrix loaded or filled with solid particulate and a liquid or low melting point metal. It will be understood that the term "liquid metal" is intended to refer to a metal or alloy having a melting point which is generally below about 90°C., although some higher melting materials may be included in the definition. The solid particulate typically forms clusters which become coated with the low melting metal and are distributed throughout the matrix. The arrangement of the present invention further provides for extrusion or oozing of portions of the loaded polymer laminae through the grid apertures. Extrusion through these apertures is achieved through application of heat and pressure to a laminae/mesh grid preform which causes the opposed laminae surfaces to merge and create a continuum of the loaded polymer. Accordingly, the continuum creates a mechanically stabilized composite thermally conductive pad which is formed without creation of additional large thermal barriers or interfaces extending along and across the thermal path. As a result, enhanced mechanical stability is achieved without sacrificing valuable properties such as high thermal conductivity and mechanical compliance.

30 [0004] Liquid metals as well as thermally conductive particulate have each been proposed for incorporation in a polymeric matrix to form thermally conductive interface pads. In the past however, the application of liquid metals for this purpose had not been widely used, primarily because of problems created instability and/or tendency of the liquid metal to oxidize or form alloys and amalgams, thereby altering and modifying the physical properties of the liquid metal component in the pad. In certain arrangements, the liquid metal component would become oxidized, both along the surface as well as in the bulk structure. By way of example, dispersed liquid metal droplets had a tendency to coalesce, a process known as Ostwald ripening, and cause macroscopic separation of the metal from the polymer matrix. In addition the oxidation of the liquid metal was sometimes accelerated upon exposure to warm and/or humid environments; this leading to the formation of brittle oxides which reduced the effectiveness of the thermal properties of the compound. Finally, while some highly thermally conductive components of prior art devices are typically electrically conductive, this property may not always be undesirable. Instability of liquid metals was believed due at least in part to the extremely high surface tension and other chemical and physical properties of the metallic component.

SUMMARY OF THE INVENTION

50 [0005] The present invention relates to thermal interface pads which employ the combination of a liquid metal with a polymer carrier. The liquid metal may either be employed as a filler by itself or preferably as a coating or encapsulant for other fillers dispersed in the polymer carrier. The filler or filler combinations may be pretreated with octyl-triethoxysilane, or other such hydrophobic surfactants, to aid in binding the surface oxide layer of the liquid metal component resulting in enhancement of overall moisture resistance. Alternatively, the silane component is blended in the polymeric matrix. The utilization of a silane such as octyl-triethoxysilane in combination with liquid metal is disclosed in co-pending application Serial No. 09/946,879, the substance of which is incorporated by reference herein.

55 [0006] The stabilized thermally conductive mechanically compliant laminate pads of the present invention employ a centrally positioned open mesh grid component comprising a grid body with generally reticulated apertures formed

therein with the apertures forming passageways or vias through which portions of the loaded polymeric resin may pass. The preparation operations for the stabilized laminate pad include positioning liquid metal/particulate containing laminae on opposed major surfaces of a grid member, and through the application of heat and pressure, causing surface portions of the laminae to flow and merge, so as to create a continuum through apertures in the mesh grid. In addition to enhancement of mechanical stability, the apertures in the intermediate mesh grid accommodate the presence of percolating clusters of liquid metal coated particles as a result of extrusion of these clusters within and through apertures. These advantages are achieved without substantially reducing or compromising desirable thermal or electrical properties while facilitating handling and utility in subsequent end use production and assembly operations.

A. The Laminae Components

[0007] In accordance with the present invention, a polymeric matrix is selected, and blended with a quantity of a liquid metal or a liquid metal and particulate combination. The polymeric matrix is preferably selected from the group of compliant compositions including waxes or hot melts. Paraffin waxes, microwaxes, silicone waxes and formulations based on these may be used. Elastomers such as silicone, natural or synthetic rubber, acrylic, polyurethane, etc. may also be used. Glassy materials such as epoxy, phenolics, may also be suitable. The polymeric matrix may be a crosslinked structure or "B-staged", including those which can be crosslinked by the user through thermal or radiative activation.

[0008] In preparing the blend with a liquid metal a high shear environment is used to break the metal into small particles. Preferably, the liquid metal comprises an alloy of indium and/or gallium, such as a gallium-indium-tin-zinc alloy, a bismuth-indium alloy or a tin-indium-bismuth alloy. Typically a metal that is liquid at room temperature or melting at a relatively low temperature, typically below 120°C and preferably below 60°C.

[0009] If a liquid metal and a particulate filler combination is used, a particulate such as boron nitride, alumina or aluminum nitride is initially dried, and thereafter placed in contact with a liquid metal. In order to appropriately wet the surfaces of the particulate, a mixture of dried particulate and liquid metal is subjected to a mixing operation until the particulate is uniformly coated with the liquid metal. While not absolutely necessary, it is desirable that the particulate be dry before blending with the liquid metal alloy. At this stage of mixing one obtains a thixotropic paste of liquid metal and the powder. One can also visualize the paste as a large percolating cluster.

[0010] Following the coating operation, the coated particulate is mixed with a blend of a liquid polymeric carrier material such as, for example, liquid silicone oil of a desired viscosity, and octyl-triethoxysilane. It is preferred that the liquid metal particulate be incorporated in the polymer blend at or near the packing limit. For liquid metal coated boron nitride, the packing fraction is typically between about 60% and 65% by volume coated particles, balance liquid silicone/octyl-triethoxysilane blend. At these volume fractions, one obtains mechanically compliant compounds that have excellent thermal conductivity due to high packing density. This improves heat transfer due to the creation of a pair of compliant laminae which are thereafter placed in superposed relationship on opposed surfaces of the grid, and subjected to heat and pressure to create a moderate force sufficient to cause opposed surfaces of the laminae to ooze through open zones of the gridwork and merge together as a continuum. Through the application of force, individual extruded portions of the opposed laminae pass into the grid apertures, and fuse or merge to create a stable continuum through the grid.

[0011] Other particulate such as aluminum oxide (alumina), and aluminum nitride have also been found to be useful when properly dried prior to contact with the liquid metal. Other combinations are possible with graphite and similar thermally conductive fillers. For the application of the present invention, the particle size should be such that the average cross-sectional thickness of particles is less than about 50 microns. As with boron nitride, this portion of the working formulation is subjected to a mechanical mixing operation which typically includes a vigorous or high-speed mixing step, with vigorous mixing being continued until a visually smooth paste is formed.

[0012] When incorporated into polymer/silane blend, it has been found that the addition of the liquid metal coated particulate effectively reduces overall viscosity. The mechanism involved in this alteration of viscosity is believed to be due to the reduction of viscous drag at the "effective particle"-polymer/silane interface. Although the liquid metal coating increases the sphericity of the configuration of the particulate, it also contributes to an effective "softness" of the otherwise hard particles. These two factors function in a mutually cooperative fashion so as to reduce both viscosity and modulus of the resulting composite. For this reason, therefore, it is desirable to control the quantity of liquid metal within the blend to the range of between about 10% and 90% by volume liquid metal, balance polymer resin/particulate. This property also facilitates and enhances passage of the formulation through the apertures or vias formed in the mesh grid.

[0013] It has been further found that the liquid metal coated particulate stabilizes and anchors the liquid metal into a three phase composite to prevent gross migration. The three phases are particle-liquid metal-polymer blend. By increasing the viscosity of the metallic phase, the tendency of metal droplets to migrate and coalesce into larger drops that could macroscopically separate and leak from the composite is severely retarded. In order to even further stabilize the structure, the techniques of the present invention are employed in order to enhance mechanical stability. Increased

stability is achieved without interposing additional thermal interfaces along and across the entire conductivity path, any one of which increases thermal impedance or resistance. Furthermore, it has been found that the liquid coated particulate provides a Bingham-plastic like character in the resultant composite, this allowing the paste to remain static in the absence of external stress, and yet conform and/or flow easily when subjected to stress. Upon application of heat and pressure, and when liquid metal is incorporated in the range set forth above, the desirable flow characterized as "oozing" of the composite occurs through the apertures formed in the grid.

[0014] Because of the tendency to undergo liquid-to-liquid macroscopic separation, liquid metals do not typically blend well with polymer liquids, including silicones. In accordance with the present invention, however, when particulate, in particular boron nitride, is initially coated with an indium or gallium alloy, the microscopic separation phenomena is reduced, with the liquid metal being supported or retained in coated particulate form. This is believed due to the increased thixotropy of the metal phase. In addition, the coated particulate, when added to the polymer/silane blend, functions effectively to form thermal vias within the composite. In certain cases, the thermal conductivity of the particulate such as boron nitride, may even exceed that of the liquid metal per se, such as, for example, that of a eutectic alloy of indium, gallium, and tin.

B. The Grid Component

[0015] The grid is preferably a thin mesh body fabricated from a highly thermally conductive metal such as, for example, copper or aluminum, although certain non-metallic materials may be used as well. The thin grid preferably has a cross-sectional thickness of between about 0.5 mil and 10 mils, with a thickness of between about 1 and 5 mils having been found to be preferable.

[0016] The grid has an array of reticulated apertures, with the size and density of the apertures creating a grid structure which is between about 10% and 90% open, balance structural. For most purposes, a grid aperture pattern with about 50% or more open is preferred.

[0017] In the event it is found desirable to utilize a non-metallic grid, such a grid may be prepared as a woven or non-woven fabric comprising graphite, carbon or glass fibers. Alternatively, certain other polymer fibers may be employed as well. It is, of course, appropriate to utilize materials of construction which are sufficiently durable for the required application. Any such non-metallic fabric (including non-woven fabrics) would likewise be provided with a reticulated pattern of apertures. It is, of course, always desirable that when non-metallic grids are utilized, the fabric be selected as one having reasonable thermally conductive properties.

[0018] As indicated, grids may be fabricated from a fabric of filaments consisting of polyethylene terephthalate (Dacron), or a polyimide such as nylon, or the like. In connection with non-metallic mesh grids, fabric comprising graphite fibers in a reticulated pattern of 50% open may also be useful. Generally, for non-metallic mesh grids, grids having thicknesses of between about 0.5 and 10 mils with open patterns of between about 10% and 90% are useful.

C. Interface Pads Incorporating the Laminae and Grid Components

[0019] Interface pads prepared in accordance with the present invention will typically have an overall thickness of between about .5 mil and 10 mils, with the thickness being based upon the application of polymeric liquid metal bearing coatings to opposed surfaces of the grid. Each of the coatings preferably has a thickness ranging from between about .5 mil and 5 mils.

[0020] Therefore, it is a primary object of the present invention to provide an improved thermal interface pad comprising a polymeric matrix material loaded with a liquid metal or a particulate material coated with a liquid metal.

[0021] It is a further object of the present invention to provide an improved method of preparing a thermally conductive interface pad which creates a thermally conductive bridge between the opposed surfaces of a heat generating semiconductor device and a heat dissipating surface, with the thermally conductive bridge comprising a three phase composite consisting of inorganic particulate, a liquid metal, and a liquid polymer/octyl-triethoxysilane blend.

[0022] Other and further objects of the present invention will become apparent to those skilled in the art upon a study of the following specification, appended claims, and accompanying drawings.

IN THE DRAWINGS

[0023]

Figure 1 is a perspective view illustrating the individual laminae and stabilizing grid arranged in accordance with the present invention;

Figure 1A is a fragmentary sectional view on a highly enlarged scale of the individual laminae and stabilizing grid arranged in accordance with the present invention;

Figure 2 is a view similar to Figure 1, with certain portions of the laminae and grid having been broken away in order to more clearly illustrate the features of the present invention;

Figure 3 is a reproduction of a photo micrograph of a cross-sectional cut-away of a thermal interface prepared and stabilized in accordance with the present invention;

5 Figure 4 is a performance graph of thermal impedance versus temperature for an interface pad fabricated and stabilized in accordance with the present invention;

Figure 5 is an elevational view, partially in section, of a typical assembly;

Figure 6 is a flow chart of the steps involved in a typical operation for preparation of interface pads in accordance with the present invention; and

10 Figure 7 is a view similar to Figure 2 and illustrating a modified form of stabilized grid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A. The Polymer Matrix

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[0024] As indicated, the polymer matrix is preferably selected from paraffin wax, microwax, and silicone waxes comprising alkyl silicones. For most purposes waxes having a melting point of about 50-60°C. have been found particularly suited for this application. It is generally desirable to utilize a polymer matrix which undergoes a phase change at a temperature of about 10°C. lower than the phase change temperature of the liquid metal alloy. For certain purposes, soft silicone polymer consisting of a reactive siloxane elastomer, acrylic syrups, epoxy resins, either crosslinked or "B-staged", polyurethane resins are found to be useful.

20

[0025] One silicone wax utilized in the formulations of the examples is GP-533 (M.P. of 60 °C.) (Genesee Polymer of Flint, MI), with these materials being, of course, commercially available. A microwax employed is that material designated as "M-7332" (M.P. of 55 °C.) available from Moore and Munger of Shelton, CT. Another polymer matrix used is a one-part soft reactive silicone elastomer available from GE Toshiba Silicones of Tokyo, Japan under the trade designation TSE-3053.

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B. The Silane Components

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[0026] Silanes and other surface active agents including titanates, zirconates and/or assorted surface active agents are preferred to improve rheology and stability of the dispersion, and particularly for creating a hydrophobic barrier. Surface treatments with surface active agents that work well for improving rheology as well as stability of the dispersion, especially against moisture, are alkyl functional silanes, such as for example octyl triethoxy silane (OTES). Another example is methyl trimethoxy (MTMS) silane. These silanes bind to the oxides on the surface of the metal particles, creating a durable hydrophobic barrier. Additionally, these silanes compatibilize the particles with the polymer matrix and reduce particle aggregation.

35

C. The Particulate

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[0027] While boron nitride is preferred, alumina (aluminum oxide) particulate and/or graphite may be advantageously employed. For example, a particulate of spherical symmetry, with a diameter of 3 microns and a BET surface area of 2m²/g. may be employed. This particulate may be blended with the liquid metal alloys and treated similarly to formulations containing boron nitride to prepare smooth coatings with thixotropic properties. Alumina has a specific gravity of 3.75 and a thermal conductivity of 21 W·m⁻¹·K⁻¹. Alumina may be blended with a selected polymer matrix and treated with octyl-triethoxysilane for the preparation of coatings pursuant to the present invention. For most applications, the volume of the combined particulates/liquid metal alloy will comprise between about 50% and 70% by volume of the interface, balance resin matrix. Also, for conductive particulate of lower density, such as graphite, the particulate/liquid metal alloy component may comprise an amount as low as about 40% of the overall combination when blended with the polymer matrix.

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D. The Metal Alloy

[0028] Alloys which are prepared for use in the present invention having the composition and melting points as follows:

50

55

TABLE I

Alloy	Indium (%)	Gallium (%)	Bismuth (%)	Sn (%)	Zinc (%)	Melting Point (°C.)
1	51		32.5	16.5	0	60
2	66.3		33.7	0	0	70
3			57	17	0	79
4	52.2		0	46	1.8	108
5	25	61	0	13	1	7

E. Specific Interface Compositions

[0029] The following compositions have been prepared utilizing Alloy 1, with numbers being by weight:

TABLE II

Formula	Matrix		Alloy 1		40 μ m Boron Nitride		OTES	
	Parts by weight	Vol %	Parts by weight	Vol %	Parts by weight	Vol %	Parts by weight	Vol %
1	100 ¹	30	1200	52	100	15	12	3
2	100 ¹	30	1800	67	0	0	10	3
3	100 ²	32	1200	50	100	15	10	3

¹ silicone wax consisting of siloxane backbones with pendant alkyl chains and having a melting point of 60°C.

² soft silicone polymer consisting of a reactive siloxane elastomer.

[0030] Compositions designated Formulas 4 and 5 are prepared substituting Alloy 2 for Alloy 1 with comparable results. Other particulates may also be employed using alumina or graphite.

TABLE IV

Formula	Matrix		Alloy 1		3 μ m Alumina		OTES	
	Parts by weight	Vol %	Parts by weight	Vol %	Parts by weight	Vol %	Parts by weight	Vol %
6	100 ¹	30	1200	59	100	8	10	3

TABLE V

Formula	Matrix		Alloy 1		Graphite		OTES	
	Parts by weight	Vol %	Parts by weight	Vol %	Parts by weight	Vol %	Parts by weight	Vol %
7	100 ¹	33	1200	60	25	4	10	3

INTERFACE PAD PREPARATION

Formula 1:

[0031] Formula 1 was applied as two coatings on opposed surfaces of a copper mesh grid having a thickness of 2 mils and a reticulated pattern of diamond apertures 70 mils long and 35 mils wide. This mesh grid had an open area of ~ 50 %, with reasonable border margins positioned on and along the surfaces. This formulation was applied to opposed surfaces, the coatings each having a thickness of 2 mils. Following application of the coatings to opposed surfaces of the mesh grid, the assembly was pressed under a unit pressure of 1-15 psi at a temperature of approximately 125° F. Thermal performance was excellent, with the thermal conductivity of the compound being

7 W-m⁻¹-K⁻¹ and thermal impedance being less than 0.2 °C-cm²-W⁻¹. In certain formulations and applications, where the coating is less viscous, it may be desirable to subject the coating to a preliminary cure operation until the "B" stage is reached.

5 Formula 2:

[0032] Formula 2 was applied as two coatings on opposed surfaces of an aluminum mesh grid having a thickness of 1.5 mils and a reticulated pattern of diamond apertures 50 mils long and 25 mils wide. This mesh grid had an open area of between ~40 and 50 %, with reasonable but narrow border margins positioned on and along the surfaces. This formulation was applied to opposed surfaces, the coatings each having a thickness of 2.5 mils. Following application of the coatings to opposed surfaces of the mesh grid, the assembly was pressed under a unit pressure of 10-15 psi at a temperature of approximately 125° F. Thermal performance was excellent, with the thermal conductivity of the compound being 3 W-m⁻¹-K⁻¹ and thermal impedance being less than 0.2 °C-cm²-W⁻¹.

[0033] Other formulations may be utilized to create thermal interface pads with results substantially similar to those reported in connection with Formulas 1 and 2 above. Thermal interface pads utilizing non-metallic grids of Dacron with openings configured similarly to those of Formulas 1 and 2 have reasonable thermal performance properties.

STRUCTURES UTILIZING THE PRESENT INVENTION

[0034] With attention now being directed to Figures 1 and 2 of the drawings, it will be noted that interface pad generally designated 10 comprises a central grid body 11 arranged medially between coating layers 12 and 13. Further, as illustrated in Figure 2, grid 11 is provided with reticulated apertures as at 15-15 which are sized so as to permit ingress or mutual oozing of coatings 12 and 13 until fused together and merged. Further, and as shown in the photomicrograph of Figure 3, following fusion and merger, thermal interface pads of the present invention create and form a continuum through the mesh, thereby eliminating internal thermal interfaces in particularly in the apertures where bridging of the opposed coating occurs.

[0035] With attention being directed to Figure 7 of the drawings, a modified interface pad consistent with the present invention is illustrated, having the same features as the modification illustrated in Figures 1-6, with the exception being that the reticulated apertures as at 15A-15A are of a different shape, specifically, a diamond-shaped configuration. The various components of Figure 7 are the same as those shown in the embodiment of Figures 1-6, with these components being designated by the same reference numeral together with the suffix "A".

[0036] With attention now being directed to Figure 4 of the drawings, it will be noted that a phase change occurs at temperatures indicated as T1 and T2. More particularly, the materials are selected for the present invention wherein the polymeric matrix at least partially fuses or undergoes a phase change at a temperature lower than that of the liquid metal component. Given the presence of the stabilizing mesh grid, overall stability of the composite is preserved. The phase change temperature differential is preferably about 10° C.

[0037] Figure 5 is provided to demonstrate the utilization of the compliant pad of the present invention in connection with a heat generating semiconductor device of conventional configuration. Accordingly, the assembly 10 shown in Figure 5, includes a heat generating semiconductor device or package illustrated at 21 having a heat sink, heat spreader, or other heat dissipating member illustrated at 22. Interposed between the opposed surfaces of semiconductor device 21 and heat dissipating member 22 is a mechanically compliant stabilized thermal interface pad 23 prepared in accordance with the present invention.

GENERAL COMMENTARY

[0038] As previously indicated, BN or alumina particulate can range in size from up to about 1 micron diameter and up to about 40 microns in cross-sectional thickness. It will be observed that the platelet-like configuration of boron nitride in particular provides a highly desirable and effective combination when wetted with liquid metal, with the effective particle being illustrated in the micrograph of Figure 3. As indicated in Figure 3, the individual laminae flow as a continuum through the openings formed in the grid, with the particulate, wetted with liquid metal, aiding in forming the interface-free continuum through the entire thickness of the pad. Viscosity control is aided by this feature.

[0039] Although the siloxanes described above are preferably utilized, silicone resins may also be utilized as a matrix. One such resin is designated "TSE 3053" from GE-Toshiba Silicones, Inc., with these materials being, of course, commercially available. Silicones having viscosities up to about 1000 centistokes may be satisfactorily utilized. The presence of the silane modifies the viscosity slightly, producing an oil composition with slightly lower viscosities.

[0040] It will be appreciated that the above examples are given for purposes of illustration only and are not to be otherwise construed as a limitation upon the scope of the following appended claims.

Claims

1. In a stabilized thermally conductive mechanically compliant laminate pad for interposing between opposed surfaces of a heat generating semiconductor device and a heat sink wherein the stabilized thermally conductive mechanically compliant laminate comprises upper and lower laminae on opposed surfaces of a central stabilizing apertured grid and with portions of said laminae extending through apertures in said mesh grid to form a continuum, said stabilized thermally conductive laminate being **characterized in that**:
 - (a) said upper and lower laminae comprise a mixture of:
 - (1) a polymer matrix;
 - (2) a quantity of low melting indium or gallium containing alloy having a melt point at about 120°C. disbursed within said polymer matrix;
 - (3) a thermally conductive particulate solid disbursed within said polymer matrix;
 - (b) said stabilizing open mesh grid comprising a grid body with an array of generally reticulated apertures formed therein, and with the structure and said grid forming between about 10% and 90% of the area of said mesh grid, balance apertures;
 - (c) each of said reticulated apertures having a cross-sectional dimension greater than about 0.5 mil;
 - (d) said polymer matrix selected from the group consisting of hot melt waxes of paraffin and silicone, elastomers of acrylic, silicone, urethane, and flexible epoxy's, and rigid resins consisting of silicone, urethane, epoxy and phenolic polymers with each polymer matrix having a melting point ranging from between about 40°C. and 120°C.;
2. The stabilizing thermally conductive mechanically compliant laminate pad of Claim 1 wherein said polymer matrix is cross linked prior to being interposed between surfaces of heat generating semi-conductor device and a heat sink.
3. The stabilizing thermally conductive mechanically compliant laminate pad of Claim 1 wherein said polymer matrix is mountingly interposed between opposed surfaces of a heat generating semi-conductor device and a heat sink while in the B-stage of cure, and thereafter subjected to a cross-linking operation.
4. The stabilizing thermally conductive mechanically compliant laminate pad of Claim 1 wherein said alloy has a melt point between about 30°C. and 90°C..
5. The stabilizing thermally conductive mechanically compliant laminate pad of Claim 1 wherein said thermally conductive particulate is selected from the group consisting of boron nitride, alumina, and graphite.
6. The method of preparing thermally conductive mechanically compliant pads comprising the steps of:
 - (a) preparing a mixture of:
 - (1) a low melting metal selected from the group consisting of gallium and indium alloys, and being in the liquid state at temperatures below 120°C.; and
 - (2) a thermally conductive particulate solid selected from the group consisting of boron nitride, aluminum nitride, and alumina;
 - (b) mechanically blending said mixture to cause the surfaces of said particulate to become wetted with said liquid alloy to form a homogeneous thermally conductive paste wherein said liquid alloy encapsulates individual of said particles comprising said particulate;
 - (c) combining said thermally conductive paste with a quantity of a flowable plastic resin material selected from the group consisting of a silicone wax having a siloxane backbone with pendent alkyl chains, and soft silicone polymers consisting of a reactive elastomer to form a thermally conductive mass, with said thermally conductive mass comprising from between about 10% and 90% by volume of metal coated particulate, balance flowable plastic resin blend;
 - (d) applying said thermally conductive mass to opposed surfaces of a mesh grid having an array of reticulated apertures to form a multi-layer preform grid of between about 10% and 90% open; and
 - (e) subjecting said preform to pressure sufficient to cause said oppositely disposed coatings to pass through said reticulated apertures to merge and form a continuum.

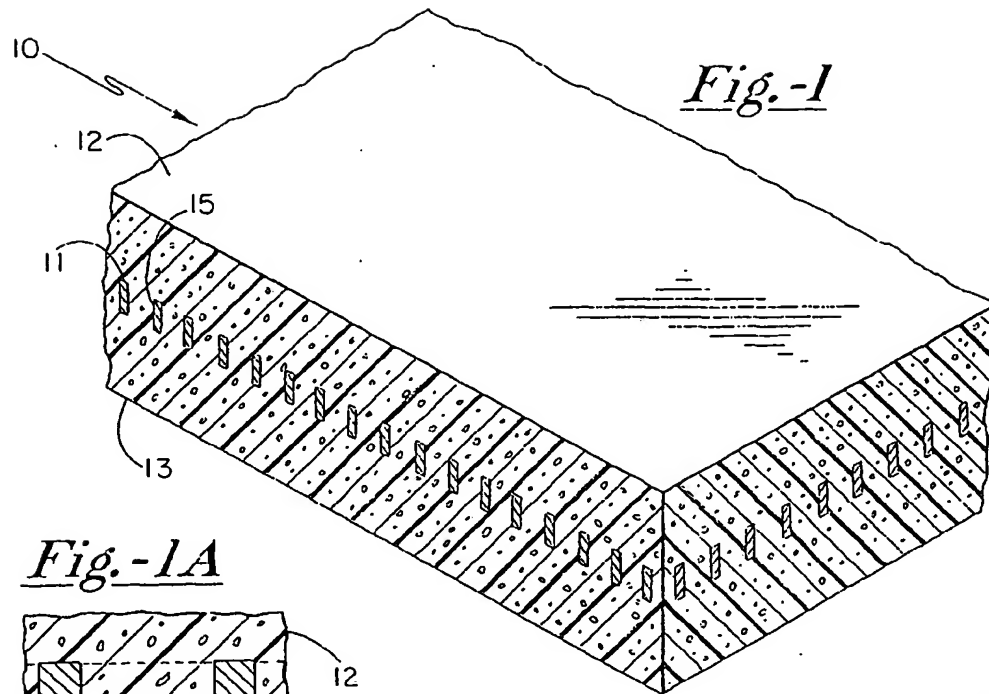
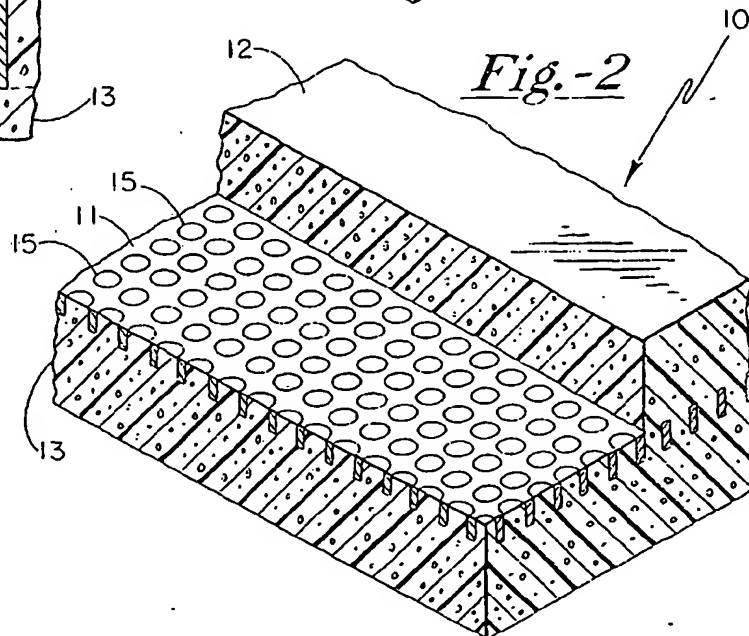
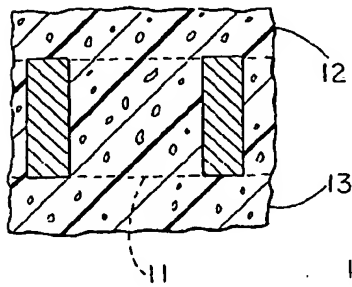


Fig.-1A



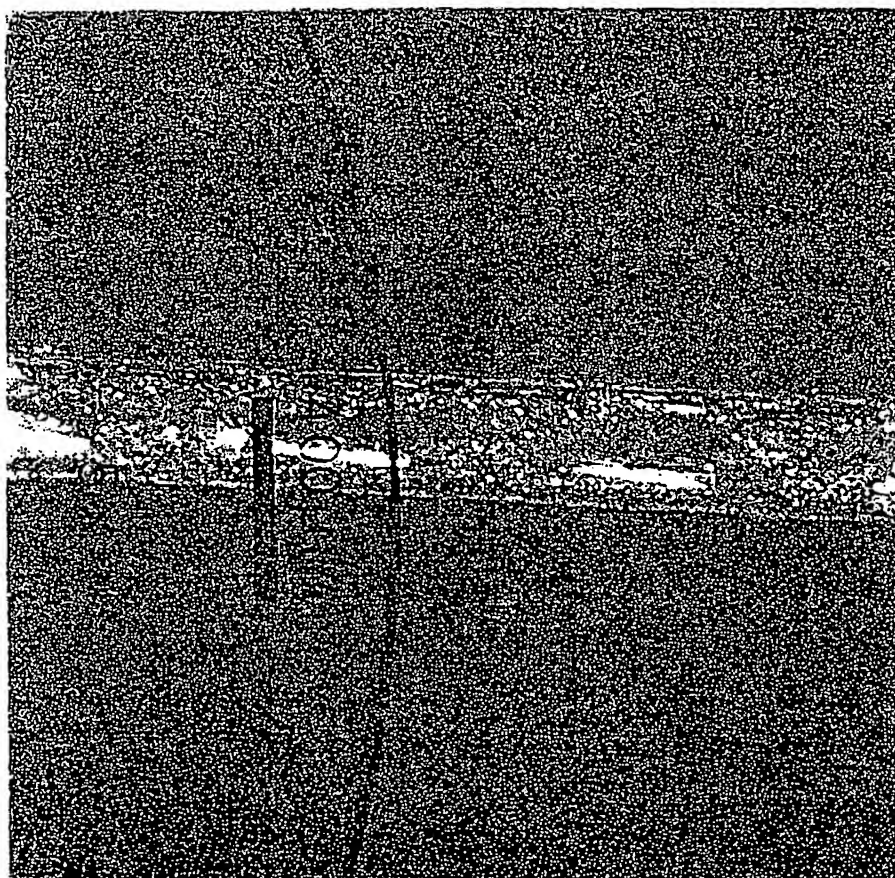


Figure 3

Fig.-4

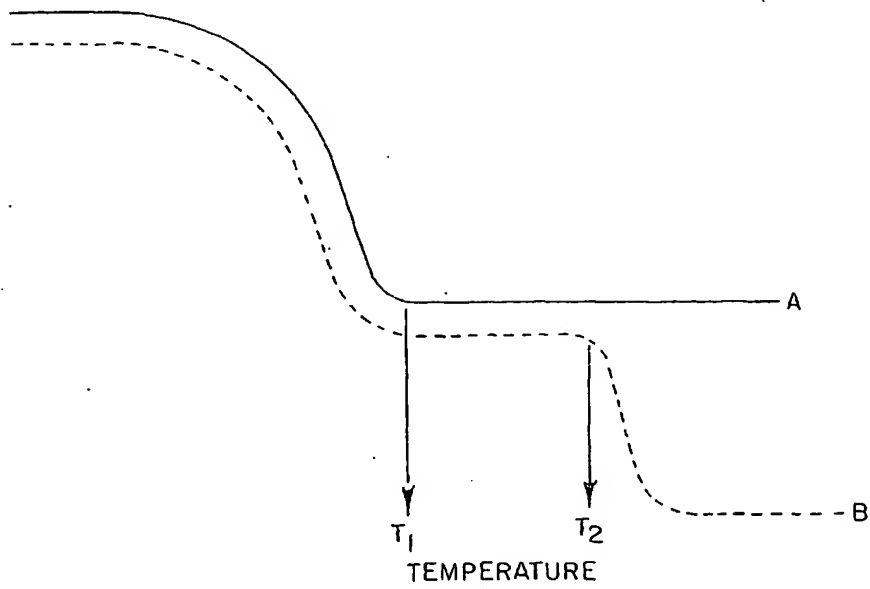


Fig.-5

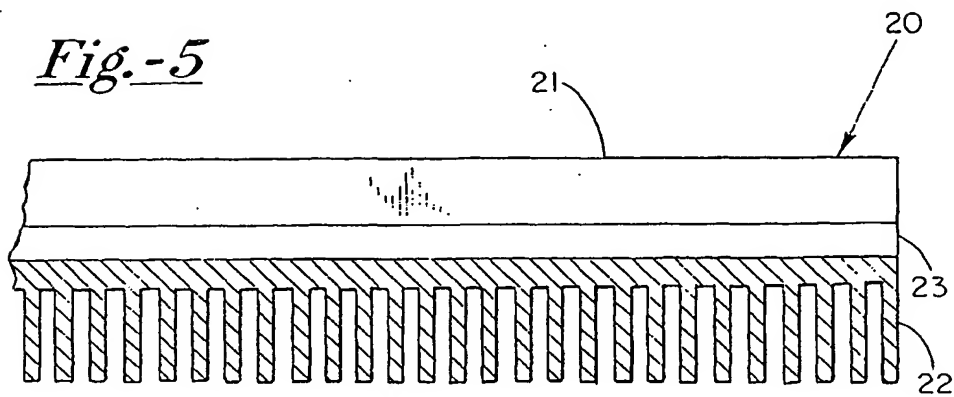
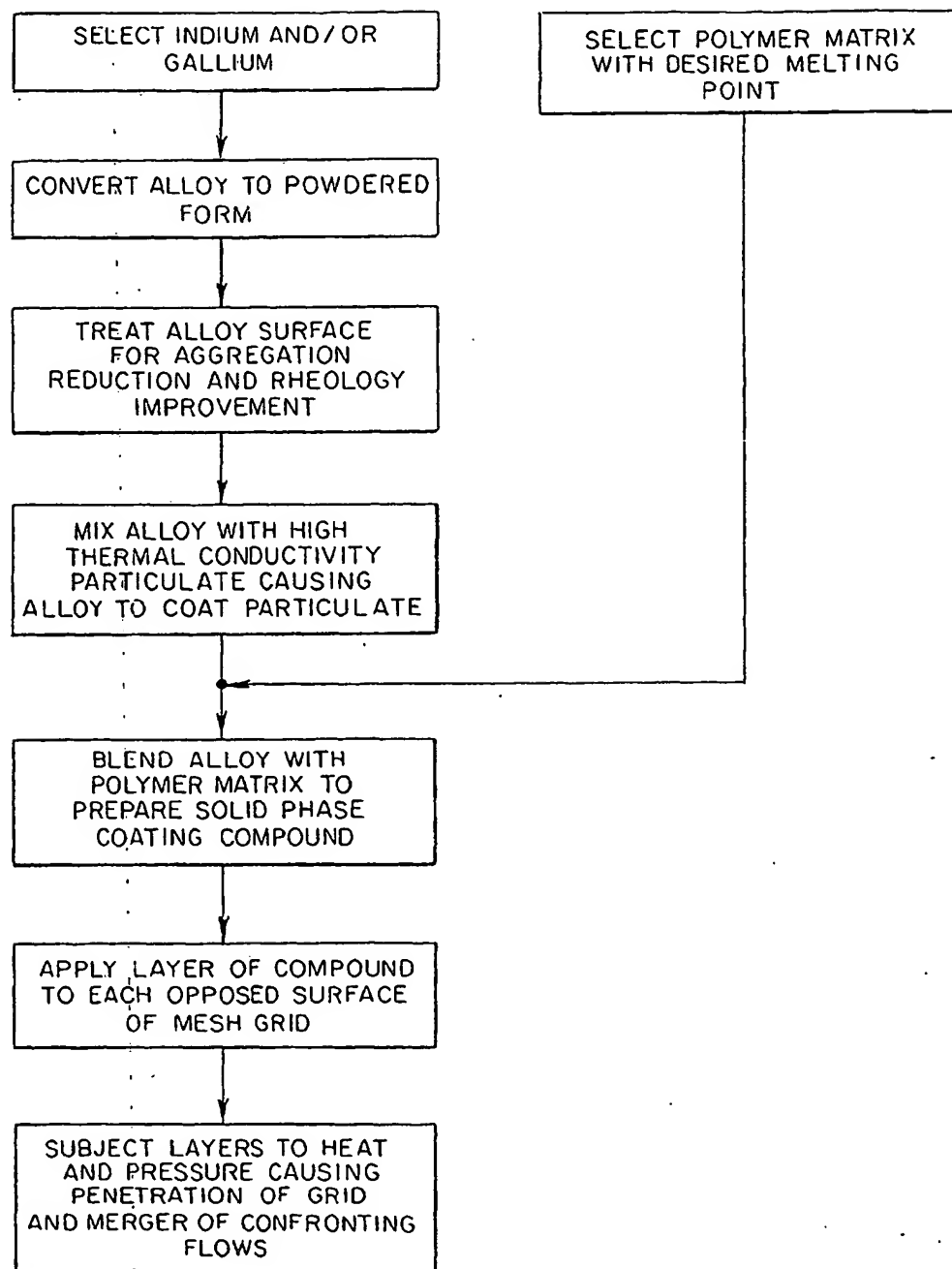
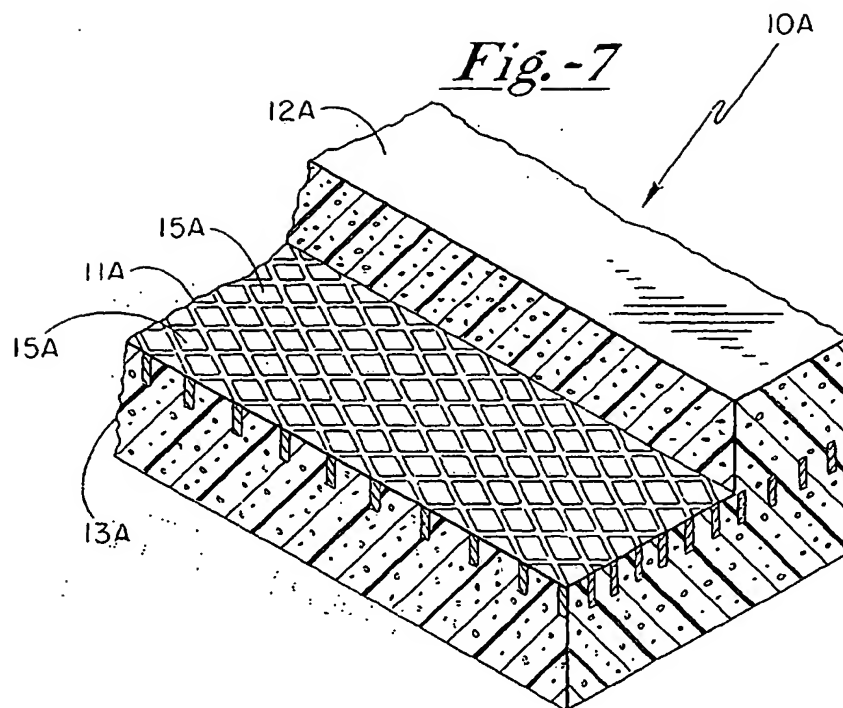
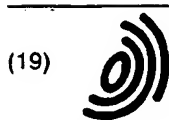


Fig.-6





(19)

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EP 1 414 063 A3

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EUROPEAN PATENT APPLICATION

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(54) Thermal interface pad utilizing low melting metal with retention matrix

(57) A stabilized thermally conductive mechanical compliant laminate pad to be interposed between opposed surfaces of a generating semi-conductor device and a heat sink, with the laminate pad comprising upper and lower laminae on opposed surfaces of a central stabilizing apertured grid. The laminae are subjected to a compressive force at an elevated temperature until portions of the laminae extend through the apertures to

form a continuum. The laminae comprise a polymer matrix having a quantity of a low melting indium or gallium alloy and a thermally conductive particulate dispersed there through, with the polymer matrix being a hot wax or melt resin. With the upper and lower laminae positioned on opposed surfaces of a central stabilizing apertured grid a compressive load is applied to force portions of said laminae to pass through apertures in the mesh grid to form a continuum.

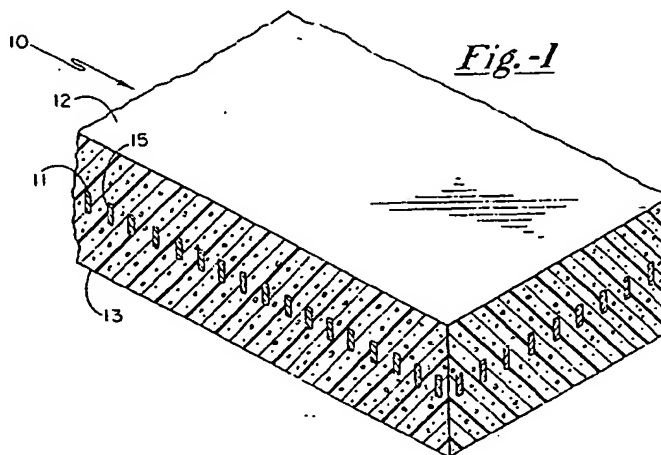


Fig. 1

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 25 5643

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IntCl.7)
Y	EP 1 143 511 A (BERGQUIST CO) 10 October 2001 (2001-10-10) * the whole document *	1-6	H01L23/373 H01L23/433
Y	US 6 165 612 A (MISRA SANJAY) 26 December 2000 (2000-12-26) * column 7, line 15-27; claims 1-11; figure 1 *	1,6 2-5	
A	* column 3, line 51 - column 5, line 67 *		
Y	US 6 015 722 A (BANKS DONALD R ET AL) 18 January 2000 (2000-01-18) * column 33, line 44 - column 34, line 33; claims 1,2; figures 14-16,26 *	1-6	
A	* column 43, line 63 - column 44, line 32 *		

A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 05, 30 May 1997 (1997-05-30) - & JP 09 001361 A (SUMITOMO SPECIAL METALS CO LTD), 7 January 1997 (1997-01-07) * the whole document *	1-6	

			TECHNICAL FIELDS SEARCHED (IntCl.7)
			H01B C09J H01L H05K C08K C08J
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 August 2004	Examiner Ley, M
CATEGORY OF CITED DOCUMENTS			
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 25 5643

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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18-08-2004

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EPO FORM P0159

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:
GENERAL ELECTRIC COMPANY
 Attn. Winter, Catherine J.
 3135 Easton Turnpike (W3C)
 Fairfield, Connecticut 06828
 UNITED STATES OF AMERICA

RECEIVED
OCT 31 2005
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NOTIFICATION OF TRANSMITTAL OF
 THE INTERNATIONAL SEARCH REPORT AND
 THE WRITTEN OPINION OF THE INTERNATIONAL
 SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference RD 124932 10/31/05	Date of mailing (day/month/year) 31/10/2005
International application No. PCT/US2005/010600	International filing date (day/month/year) 29/03/2005
Applicant GENERAL ELECTRIC COMPANY	
Action Due 11.14.05 Attorney CJD Logged By D. Hout ID 3105	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:
 The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO, 34 chemin des Colombettes
 1211 Geneva 20, Switzerland, Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

Shortly after the expiration of **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

The applicant may submit comments on an informal basis on the written opinion of the International Searching Authority to the International Bureau. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established. These comments would also be made available to the public but not before the expiration of 30 months from the priority date.

Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until **30 months** from the priority date (in some Offices even later); otherwise, the applicant must, within 20 months from the priority date, perform the prescribed acts for entry into the national phase before those designated Offices.

In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months.

See the Annex to Form PCT/IB/301 and, for details about the applicable time limits, Office by Office, see the *PCT Applicant's Guide*, Volume II, National Chapters and the WIPO Internet site.

Name and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Alex Schmidt
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NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

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